



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶:

C01F 11/18

A1

(11) International Publication Number:

WO 96/23728

(43) International Publication Date:

8 August 1996 (08.08.96)

(21) International Application Number: PCT/FI96/00058

(22) International Filing Date: 30 January 1996 (30.01.96)

(30) Priority Data:

950411

30 January 1995 (30.01.95)

FI

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(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

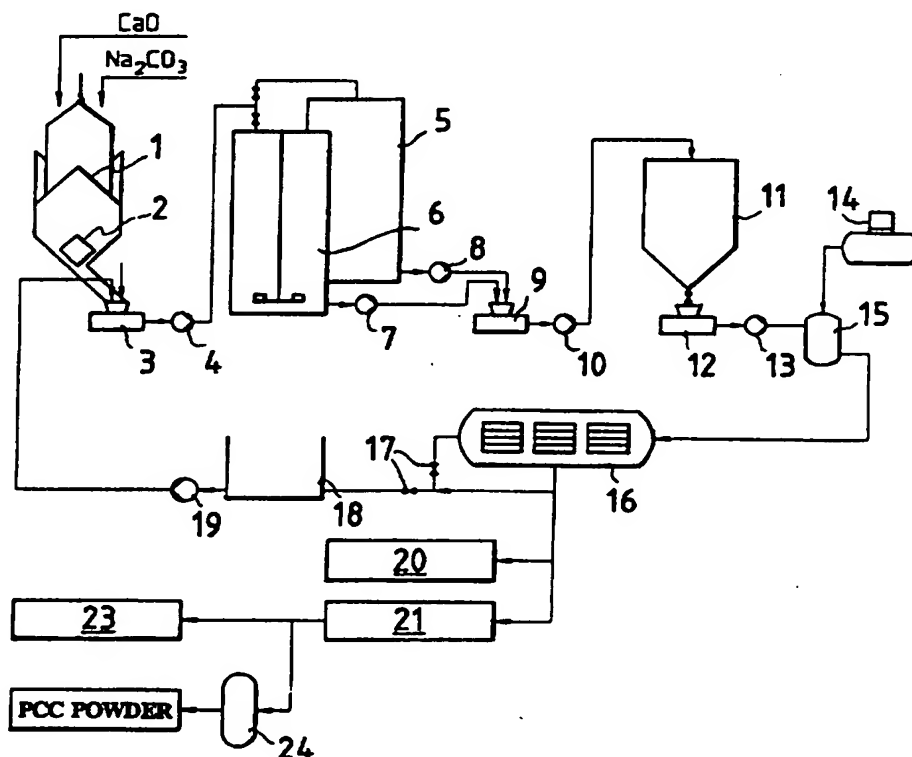
Published

With international search report.

(54) Title: PROCESS AND APPARATUS FOR PREPARING CALCIUM CARBONATE

(57) Abstract

The present invention concerns a process and an apparatus for preparing calcium carbonate. The process comprises reacting a calcium oxide raw material, which contains at least some hydrated calcium oxide, with carbonate ions in an aqueous medium for preparing precipitated calcium carbonate. The calcium carbonate is separated from the suspension and subjected to further treatment for preparation of the desired end product. The invention is characterized in that at least 80 % of the particles of the hydrated calcium oxide have a particle size of less than 3 μm and the reaction is allowed to proceed without mixing the reaction mixture. When a pigment suitable for paper coating, having a particle size of 0.2 to 0.4 μm , is to be prepared, the carbonation reaction is allowed to continue for 20 to 25 minutes before it is interrupted in an impact mixer (12).



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Process and apparatus for preparing calcium carbonate

5 The present invention concerns a process in accordance with the preamble of claim 1 for preparing calcium carbonate, in particulate calcium carbonate having a controlled crystal structure.

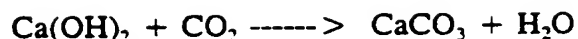
10 According to such a process, calcium carbonate is produced by reacting a calcium oxide-based raw material, which contains at least some hydrated calcium oxide (i.e. calcium hydroxide), with carbonate ions in an aqueous medium in order to produce an aqueous suspension containing calcium carbonate, and then separating the precipitated calcium carbonate from the suspension and subjecting it to post-treatment in order to produce the desired end product. When the carbonate ions are derived from sodium carbonate, sodium hydroxide can be recovered from the suspension, if desired.

15 The present invention also concerns an apparatus according to the preamble of claim 21 for preparing calcium carbonate.

20 Synthetic or industrial or precipitated calcium carbonate, which in the following will be referred to by the abbreviation PCC (Precipitated Calcium Carbonate) is becoming more and more used as a filler and mixing pigment in the chemical, pharmaceutical, polymer and paper industry and as a coating pigment for paper. With an increasing use and a larger number of applications more stringent requirements are also set on the properties of the product. The most important product properties of synthetic calcium carbonate for different applications are related to the crystalline form and crystal dimensions of the crystallized product. Furthermore, for many applications it is preferable to have a narrow crystal size distribution, i.e. the crystals should be of the same size.

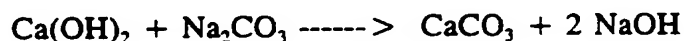
30 Calcium carbonate for the paper industry is most commonly prepared in plants known as satellite plants, i.e. facilities at a paper mill site. The process of these plants is based on the following reaction:

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Thus, an aqueous suspension (lime milk) containing slaked lime is carbonated with carbon dioxide from, for example, flue gases or off-gases from lime burning kilns. The product obtained comprises calcium carbonate and water.

Before the chlorine-alkali-process based on electrolysis became common, sodium hydroxide was prepared by causticizing of soda and lime by the well-known causticizing reaction:



In addition to sodium hydroxide, also (precipitated) calcium carbonate was then obtained.

For ecological reasons, the global production of chlorine and caustic soda is in imbalance; the use of chlorine is steadily declining and the use of caustic soda constantly increasing by and by. As far as the production of sodium hydroxide is concerned, this development has diminished the economical importance of the chlorine-alkali-process and, correspondingly, made the causticizing reaction more interesting. Thus, causticizing processes have been built in the recent years in areas, wherein, for example, natural soda (sodium carbonate) is available. However, in all of these processes, lime is constantly circulating via the mesa oven and the only product obtained is lye (caustic soda).

In summary, it can be stated that there is a need for a combination of carbonation and causticizing so as to provide for simultaneous production of caustic soda and calcium carbonate by one process. However, in practice, the above-described process combination has so far not been successfully achieved to produce high-quality precipitated calcium carbonate (PCC) suitable for use as a filler or pigment.

In all processes, wherein a crystallizing product is being produced, the provision of the

right crystal size distribution is found to be problematic. Thus, for instance, in the work "Pigment Handbook" (ISBN 0-471-82833-5) from 1987, it is stated that by precipitation of lime and soda there has never been achieved a uniform, controllable crystal size distribution. The same problems also appear in connection with PCC preparation based on carbonation with flue gases. However, it has been found that the more intensive and continuing the mixing is, the better the crystal size distribution will become.

The specific problems of the causticizing process have been the diluency of the caustic soda prepared, the cost of the separation of the PCC crystals from the soda solution, and the agglomeration of the produced crystals. As regards the concentration of the soda, it should be pointed out that in the first stage of the reaction it is necessary that the reaction medium be diluent enough in respect of the reactants so that the equilibrium of the causticizing reaction is proper. When the concentration of the soda and of the corresponding caustic soda are small (dilute medium), rather complete reaction is achieved, although fully complete reaction will never be obtained. There is always left some uncausticized soda in the lye solution and some of the lime will remain in the hydroxide form.

A process which would solve all the above-mentioned problems is not available.

U.S. Patent Specification No. 3,268,388 discloses a process embodiment, which aims at the production of pure, white PCC by causticizing. According to the process, most of the reaction is carried out when the precipitated carbonate and still unreacted lime hydrate (calcium hydroxide) are in a filter, from which the lye formed can be removed and new pure soda can be introduced instead. According to the patent specification, the process will produce particles with particles sizes of even $0.7\ \mu\text{m}$, but not even this method will provide a uniform, controllable distribution of the particle sizes.

It is further known in the art that dry slaking methods will produce finer crystals of the slaked lime than the wet process, wherein the crystals of the slaked lime tend continuously to grow larger, which is a disadvantage for the causticizing process. Wet

slaking is, however, preferred for PCC processes, because it will provide a means for easy separation of sand and coarse particles from the dilute lime milk by the use of a hydrocyclone.

5 It is an object of the present invention to eliminate the problems related to the prior art and to provide an entirely novel solution for preparing calcium carbonate.

10 The invention is based on the idea that it is possible to prepare finely divided calcium carbonate having uniform particles sizes by carbonation or causticizing, if also the particles of the calcium hydroxide are of uniform size and, preferably, only 50 times greater than the calcium carbonate particles. Preferably, according to the invention, at least about 80 % of hydrated calcium oxide particles, which are reacted with the carbonate ions, are smaller than about 3 μm .

15 Another characteristic feature of the invention is that the reaction between the calcium hydroxide and the carbonate ions is allowed to take place essentially without any mixing of the reaction mixture until the desired particle size of the calcium carbonate is achieved. The reaction is then interrupted after a predetermined time by subjecting the reaction mixture to strong mixing forces. The length of the selected time is determined
20 by the desired size and form of the produced particles.

In particular, the process according to the invention is mainly characterized by what is stated in the characterizing part of claim 1.

25 The apparatus according to the invention is, again, characterized by what is stated in the characterizing part of claim 21.

Some features of the apparatus are disclosed in the characterizing parts of dependent claims 22 to 26.

30 According to a preferred embodiment of the invention, PCC suitable for paper coating is produced, the particle or granular size of which is in the range: $0.2 \mu\text{m} < \varnothing < 0.4$

μm . It has been found that this granular or particle size will give CaCO_3 crystallization seeds, which have a ratio of diameter to length of about 1. This kind of spherical crystals are very well suited for paper coating because they fit well into the pores on the surface of the paper due to their small size. The crystals also have a high light scattering efficiency, which makes it possible substantially to improve the brightness of the paper by using the calcium carbonate crystals prepared according to the invention. When the crystals grow larger in particle size than 0.2 to 0.4 μm , they grow more rapidly in length than in thickness (or diameter), which makes the calcium carbonate crystals needle-like. Needle-like crystals do not fit as well into the pores of the paper and they do not, therefore, work as filler as well as spherical crystals.

It is possible to obtain the desired granular size by carbonating calcium hydroxide whose particles are smaller than 3 μm . In order to prevent the crystals of the slaked lime from growing too much, it is preferred to carry out the contacting of the slaked lime and soda and/or carbon dioxide as soon as possible after the slaking of the calcium oxide. In particular, it is preferred to bring slaked lime and soda in contact with each other, for the forming of crystallization seeds, in a rapidly rotating mixer, which generates rather strong mixing and shear forces. A mixer suited to this use is, for example, comprised of an impact mixer, which is described below. In the present application, the initial contact of slaked lime with soda is also called "pre" or "initial mixing".

After premixing the crystallization seeds are allowed to grow without disturbance until their sizes are of the desired order. By the expression that the reaction mixture is essentially not mixed (or that the mixture is not "disturbed") is meant that the reaction mixture is not subjected to any turbulent mixing forces. In practice the reaction is carried out in a reaction tank, to which the reaction mixture is fed from above and wherein the gelled sediment or precipitation containing calcium carbonate is settling during the reaction time down towards the bottom of the tank, which movement will generate laminar flows within the reaction mixture. These flows will not, however, disturb the formation of crystal seeds.

After a preselected time the carbonation reaction is interrupted by mixing the mixture so intensively that at least a part of the calcium carbonate crystals formed in the reaction mixture are broken up. Preferably this interruption is effected with an efficient mixer by using strong turbulence and impact and shearing forces. It is particularly preferred to use an impact mixer for this purpose as well.

The preparation of a calcium carbonate product suitable for use as a paper filler takes some 15 to 35 minutes, typically about 20 to 30 minutes. It has been found that when the mixture is disturbed before the end of said time and before the crystals have grown to the size 0.2 to 0.4 μm , there are present abundantly crystals, which are smaller than 0.2 μm in particle size and which are not preferred for the preparation of paper pigments.

The term "impact mixer" as used in the present context denotes an apparatus equipped with rotating rotors provided with plate-like impact stops which generate an over-sized shear force (after the impact) which causes the liquid and suspension to flow in the direction of the centrifugal force from the impact stops on the inner mixing rotor to the impact stops of a concentric outer rotor, rather large shear forces being directed towards the mixture when it flows from one impact stop to another. These shear forces are caused by the fact that the vanes of successive rotors have different speeds and rotating directions. An apparatus of this kind uses vanes or plates which are either radial or slightly inclined in the rotational direction. An impact mixer will make it possible to perform uniform mixing, and the shearing force resulting from the impacts between the solid matter and the solid impact surfaces is more even and uniform, statistically calculated, than in other types of mixers. Typically over 95 % of the material flux obtains almost 100 % of the maximum impact energy and only 5 to 10 % gets less than 60 % of the maximum impact energy. The variation of the intensity of the mixing turbulence is many times greater for all other types of mixers, even for the dissolver type "high-shear" mixers. Because of the afore-mentioned reasons, renewed disintegration of the aggregates and flocs formed is almost total in comparison to a conventional mixer.

The impact mixer can also be used for slaking of calcium oxide, as the detailed description given below will show. According to one embodiment, calcium oxide containing raw material containing at least a part of hydrated calcium oxide, is produced by grinding calcium oxide first to a granular size of less than 200 times the diameter, which is set as the upper limit for 80 % of the crystals of the slaked lime. The calcium oxide is slaked by mixing it in water, the mixture formed by the calcium oxide and water being subjected to strong shear forces during mixing.

When a narrow crystalline size distribution of the carbonate product is sought, the crystallization reaction of the CaCO_3 is initiated, continued and finished on the surface of each uniformly sized Ca(OH)_2 particle as simultaneously as possible by initiating the reaction with rapid turbulent mixing (e.g. by using an impact mixer), the reaction is continued by leaving the mixture essentially unmixed during the reaction time in a tank, wherein the particles can be formed in as homogeneous conditions as possible, and after the reaction time a turbulent postmixing is carried out in order to avoid smaller CaCO_3 particles than desired.

According to one preferred embodiment, the process according to the invention is implemented as a causticizing process, which comprises the simultaneous preparation of both paper coating grade PCC (rhombic calcite) and a ready-to-use caustic soda solution for the process of a pulp mill. According to this embodiment the carbonate ions are brought to the reaction with calcium hydroxide in the form of, e.g., a sodium carbonate solution. Alternatively, a part — even the main part — of the carbonate ions can be introduced into the process with flue gas or as pure carbon dioxide and preferably only the initial nucleation is carried out by soda and the obtained caustic soda is left in solution as a dispersion adjuvant, whereby filtration only comprises concentration of the slurry, if needed.

The carbon dioxide obtained from flue gases can preferably also be introduced by first binding it to NaOH to form Na_2CO_3 and then contacting this matter with Ca(OH)_2 . The formed NaOH or a part thereof is returned to the gas absorber.

The NaOH produced by the invention can be used as such in a pulp mill or it can be sold for other purposes after concentration, e.g., by evaporation, .

5 The process equipment described makes it also possible to regulate the ratio between the formed calcium carbonate and NaOH by feeding carbon dioxide containing gas or pure carbon dioxide into the impact mixer of the process, if the need for caustic soda is smaller than the equivalent amount of the corresponding calcium carbonate. The gas feed to said impact mixer is facilitated by the fact that the operational space of the mixer is mainly empty during the use of the mixer. By varying the component ratios of
10 the mixture the concentration of the NaOH solution can be set at 6 to 15 %, which means that it is ready to be used in the processes of most pulp mills.

The present invention provides considerable advantages. Thus, the process has been designed so that the PCC can be prepared as easily as possible and by using as simple
15 equipment as possible. The process and the apparatus according to the invention are suitable for forming calcium carbonate both by the causticizing reaction and by flue gas carbonation, while ensuring in both cases an extremely narrow crystal size distribution and the means for regulating it. The process according to the invention excellently fulfilled the set requirements during our tests, but surprisingly it has been found that
20 the process is suitable for controllable preparation of other crystalline forms of calcium carbonate (aragonite/calcite) and other crystalline sizes thereof by the causticizing process as well. This is also possible when the preparation process employs gas carbonation in addition to the caustification process or instead of it. The crystalline form of the produced calcium carbonate is preferably controlled by regulating the
25 process temperature to below +42 °C, when calcite crystals are to be prepared, and above +43 °C, when aragonite crystals are produced.

Next, the invention will be described in more detail with the aid of the attached drawing and photographs, whereat
30 Figure 1 indicates the process scheme for a preferred embodiment of the invention, Figures 2 to 8 comprise electron microscope micrographs taken of the reaction mixture at different points of time (the times are calculated on basis of the premixing).

The most important steps of our invention are the slaking of the lime, carbonation, the interruption of the carbonation and the filtration, which are described in the following with reference to Figure 1.

5 1. Slaking of lime

Slaking of lime for the causticizing (and/or gas carbonation) is preferably continuously performed, depending on the need of the slaked lime, a relatively short period of time before the initiation of the carbonation. The slaking of the lime comprises the following steps:

10 The starting material, CaO, is fed via the feed hopper 1 to pregrinding 2, for example to a vibratory cone crusher (crushing ratio preferably 2 to 8, in particular about 5), which is used for grinding the CaO to desired fineness, with a maximum granular size of preferably 5,000 to 15,000, in particular $< 10,000$, times the aimed crystal size of the end product carbonate.

20 The preground CaO is fed with water to, for instance, an impact mixer/slaking apparatus 3 of the ATREX type, which within a short residence time (preferably < 1 second) subjects each unit volume of the components which are to be mixed to a spread of shear forces of essentially uniform intensity under strong turbulence. According to our investigations, of the calcium hydroxide crystals which are generated in this way, at least 80 % have a diameter which is less than $1/200$ of the maximum size of the preground CaO even after 24 hours from the initiation of crystallization. Since the

25 solubility of slaked lime in water is only about 2 g/liter, the size of the calcium hydroxide crystal means, in the present context, the size of the insoluble solid particle in the aqueous suspension, as expressed by an approximate value for its mean diameter.

30 The calcium oxide-based aqueous slurry obtained from the slaking (lime milk) is pumped 4 to an intermediate tank 5.

The sodium carbonate solution used for carbonation can be prepared in the same

apparatus as the calcium carbonate. The break tank for the aqueous solution of sodium carbonate is given the reference number 6.

2. The carbonization reaction

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Because it is an aim to achieve as small and uniformly sized crystals of slaked lime as possible, which crystals can then be used as a raw material for the carbonate to be prepared, the CaO has to be preground, slaked as soon as possible and reacted with soda (and/or carbon dioxide) so that the calcium hydroxide crystals formed do not have time to grow too big or to agglomerate.

10

The crystallization of CaCO_3 is initiated as simultaneously as possible throughout the whole process batch by bringing the surfaces of the Ca(OH)_2 particles and the Na_2CO_3 solution (and/or CO_2) in immediate mutual contact by means of efficient initial mixing. Preferably, this is again achieved with the help of an ATREX type impact mixer 9 or a similar apparatus, for which it is typical that when the mixer is treading in its mixing chamber in comparison to its total volume very small amounts of mixture at a time and very quickly (residence time < 1 second), the vanes of the mixing rotors of the impact mixer subjecting each particle with a probability great enough to the necessary mixing energy for immediately initiating the carbonation reaction.

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By using the dosing equipment or batcher of the premixer (pumps 7, 8) it can be ensured that the weight ratios of the substances needed for the reaction are proper, and also the dosing of the gas to the reaction can be carried out in connection with the premixing. The gas dosing is not shown in Figure 1. A strong turbulence during premixing ensures simultaneous initiation of the growth of carbonate crystals.

25

The premixing produces a reaction mixture, which contains hydrated calcium oxide stemming from the calcium oxide-based starting material and carbonate ions. It is fed into the PCC reactor 11 from above. The reactor comprises a cylindrical tank whose longitudinal axis is vertical and lower end is conical.

30

The reaction time in the reactor 11 depends on the desired crystal size of the final product; for coating PCC prepared from $3\text{ }\mu\text{m}$ \varnothing $\text{Ca}(\text{OH})_2$ it takes some 20 to 25 minutes to prepare CaCO_3 with a diameter in the range of $0.2\text{ }\mu\text{m} < \varnothing < 0.4\text{ }\mu\text{m}$. According to the invention, the mixture is essentially not mixed after the initial mixing. Instead, the carbonate crystals are allowed to form without disturbance as the surface layer of the $\text{Ca}(\text{OH})_2$ particles continuously reacts with the surrounding soda solution until, when the whole hydroxide particle has reacted, the carbonate crystals formed on its surface have reached the desired size. If the reaction is allowed to proceed long enough the ready carbonate crystal will separate from each other, while the other product produced by the process, viz. NaOH , works as a dispersion medium and keeps the formed crystals separated from each other.

The tests we have carried out clearly show that the mixture will form a gel after about 5 minutes of reaction (cf. the example described below), when the carbonate crystals formed on the surface of the hydroxide "parent particles" have grown so large that they fill up the spaces between the $\text{Ca}(\text{OH})_2$ particles, thus increasing the viscosity of the mixture (later: viscous reaction stage). The surprising finding that the carbonate crystal disperse after the "parent particles" have been wholly consumed, when the reaction proceeds far enough, manifests itself in our test in that the mixture becomes liquid.

This phenomenon has not been observed or correctly understood in the prior art processes, because, as far as we are aware, the prior art has attempted to prevent this "gelling" by continuing the mixing during the whole reaction, a part of the freshly formed carbonate crystals being continuously broken, which enlarges the crystal size distribution to include more finely divided material. Thus, the possibilities of producing easily filtered CaCO_3 crystals, which are uniform in particle size, are lost.

The crystalline form of the prepared calcium carbonate depends on the temperature of the crystallization. Calcite crystals are formed at temperatures below $42.5\text{ }^\circ\text{C}$ and typically more oblong aragonite crystals at higher temperatures. In order to control the crystalline form, the apparatus 11 is equipped with heat regulation means. This is important also for the reason that the use of small $\text{Ca}(\text{OH})_2$ particles and the efficient

initial mixing by using an impact mixer will increase the heat generation during the process.

3. Interruption of carbonation

5

After the desired reaction time the reaction mixture is removed from the reactor 11 and conducted to a mixer 12 for interruption of the carbonation. This measure, which is also called post-mixing, is preferably carried with an impact mixer 1 to 4 times, because it is possible by the post-mixing to react unreacted $\text{Ca}(\text{OH})_2$ with the already existing CaCO_3 particles. By selecting the point of time for the post-mixing, it is possible to regulate the form and maximum size of the produced crystals. In this way the formation of under-sized carbonate crystals generated by reaction residues can be avoided. Based on our test results and also pursuant to a theory, known as Kormogorov's and Hinze's law, which relates to the mixing length of turbulence, the post-mixing performed by an impact mixer helps to keep the crystal size distribution narrow because the mixing only increases the size of such particle agglomerates which it is incapable of disintegrating. In connection with the post-mixing, the reaction can be enhanced by dosing carbon dioxide into the mixture, if the mixture does not contain enough dissolved free soda or if the NaOH concentration in the mixture becomes too high for the causticizing reaction to proceed in the desired direction.

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4. Filtration

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From the mixer 12 the mixture is pumped 13 to a tank 15, to which pressurized air is pumped from a storage tank 14. The mixture is conducted with the pressurized air to a filtration unit 16. The filtration can be carried out by using a cassette-type pressure filter 16 provided even with very fine filtration cloths, because the size distribution of the CaCO_3 crystals produced is so narrow that the cloths do not form dense overlapping plates, but the NaOH filtrate can always be pressed through them.

30

It is preferred to carry out the filtration by pressurization using pressurized air in order to avoid excessive dilution of the filtrate, i.e. usually the aqueous sodium hydroxide

solution.

The sodium hydroxide solution is recovered and conducted to the vessel 20.

5 The pressure filter is washed with water and the PCC slurry is conducted to the intermediate storage tank 21, from which it can be further conducted to storage tank 23. For the preparation of PCC powder, at least a part of the slurry can also be dried in a dryer 24.

10 The rinsing water, which contains some PCC and sodium hydroxide is recirculated to the slaking of calcium oxide.

15 In the following, the process according to the invention and the process apparatus preferably used for implementing the process will be examined in more detail with the aid of a working example and the attached micrographs relating to the simultaneous preparation of coating PCC and NaOH, which is the embodiment most studied by us.

Example

20 The following test shows the working of the invention on laboratory scale.

Test arrangements:

- 25 1. Slaking of lime: CaO . Ø 10 mm, was preground in a vibratory cone crusher to a diameter of < 2 mm. The slaking was carried out in an ATREX-mixer at a temperature of 75 to 80 °C at a solids content of 12 %. The $\text{Ca}(\text{OH})_2$ was allowed to post-slake in a tank for about 20 h.
- 30 2. The Na_2CO_3 was dissolved in water at a temperature > 30 °C, in order to prepare a saturated solution with a concentration of about 32 %.
3. The causticizing process was carried out in a laboratory at the Technical University

of Helsinki, equipped with an electron microscope for monitoring the progress of the process. However, at the laboratory, no ATREX mixer was available for achieving the initial mixing. Because the amount of mixing components was small (Ca(OH)_2 mixture, 50 g, and Na_2CO_3 solution 23.5 g) the process could, however, be initiated simultaneously enough throughout the whole mixture by using a laboratory mixer for the initial mixing of the components.

4. The temperature during the whole reaction stage was maintained at $< 30^\circ\text{C}$. The process components were inspected with an electron microscope after 5, 15, 19, 22, 25, 29, 39 and 60 minutes from the start of the causticizing reaction. Before the reaction, the Ca(OH)_2 raw material was also inspected with the aid of an electron microscope.

Test results:

The main stages of the process:

Figure 2 — the Ca(OH)_2 particles are relatively separate, granular size about $2 - 4\ \mu\text{m}$ \varnothing .

Figure 3 — after about 5 minutes the mixture begins to arrange as a uniform viscous mixture with detectable particles having a \varnothing of about $2\ \mu\text{m}$.

Figure 4 — about 25 minutes: The particle sizes are $0.2 - 0.4\ \mu\text{m}$, post-mixing is initiated.

The electron microscope micrographs of the intermediate stage of the reaction indicate the rapid change of the composition of the reaction mixture:

Figure 5 — about 15 minutes: The particles are still distinguishable as spherical particles, which have a rough surface and are adhering to each other: the viscosity of the mixture is high.

Figure 6 — about 19 minutes: A uniform gelled mass, with lumps of a size of about $2\ \mu\text{m}$ \varnothing .

Figure 7 — about 22 minutes: A uniform gelled mass, with hardly any distinguishable particles.

Electron microscope micrographs of the situation which will prevail when the reaction is allowed to continue even after 30 minutes.

Figure 8 — about 39 minutes: Rod-shaped crystals, \varnothing 1 - 2 μm , length 5 - 10 μm , are beginning to form in the gel (Figure 8).

Figure 9 — about 43 minutes: The crystals which can be seen in the previous micrograph disintegrate

Figure 10 — about 60 minutes: CaCO_3 is primarily in soda solution in the form of rod-shaped crystals with lengths in the range from 5 to 20 μm and having a diameter of 2 μm , and in the form of granular crystals with a diameter of 0.1 to 1.0 μm .

The test shows that when the caustification process is interrupted according to the invention, e.g. during the preparation of coating PCC (0.2 to 0.4 μm \varnothing) 15 to 25 minutes from the initiation of the reaction with the aid of efficient ATREX mixing, the desired end result is obtained by homogenization of the mixture, as the crystals formed in the gel are dispersed by the NaOH formed and when the loose agglomerates in the gel are broken up.

The test further showed that during the high-viscosity stage of the reaction, i.e. within about 5 to 15 minutes from the beginning of the reaction, mixing of the mixture is not necessary. From this it can be inferred that, in addition to the great energy consumption of mixing, it would not be advantageous to mix the mixture also because mixing of the forming $\text{NaCO}_3 + \text{Ca}(\text{OH})_2$ gel with the generated NaOH would slow down the growth of the CaCO_3 crystals to the desired size and therefore leave too much extremely small PCC crystals in the product, which will make filtering more difficult.

It also appeared that the crystals become oblong in the gel unless the reaction is interrupted by means of an efficient post-mixing. This confirms the fact that the process according to the invention can be regulated by timing the post-mixing so that PCC

crystals of varying shapes and sizes are produced at the desired size distribution.

Claims:

1. A process for preparing calcium carbonate, according to which process
- a calcium oxide raw material, which contains at least some hydrated calcium oxide, is reacted with carbonate ions in an aqueous medium in order to prepare calcium carbonate,
 - the initial concentrations of calcium oxide, hydrated calcium oxide and of the carbonate ions is being maintained so high that calcium carbonate is precipitated into the medium, whereby an aqueous calcium carbonate-containing suspension is being formed, and
 - the precipitated calcium carbonate is separated from the suspension and subjected to further treatment for preparation of the desired end product,

characterized in that

- at least about 80 % of the particles of the hydrated calcium oxide subjected to the reaction have a particle size of less than about 3 μm ,
- the reaction is allowed to proceed essentially without mixing of the reaction mixture containing hydrated calcium oxide and carbonate ions, and
- the reaction is interrupted after a predetermined time by applying mixing forces to the reaction mixture.

2. The process according to claim 1, wherein the hydrated calcium oxide particles brought to the causticizing reaction have a particle diameter which, at the most, is 50 times the maximum particle size of the produced calcium carbonate.

3. The process according to claim 1 or 2, wherein calcium carbonate is prepared, mainly having a particle size of 0.2 to 0.4 μm .

4. The process according to claim 3, wherein at least about 80 % of the particles of the hydrated calcium oxide subjected to the reaction have a particle size of less than 10 μm .

5. The process according to any of claims 1 to 4, wherein the carbonation reaction is

interrupted by mixing the mixture so vigorously that at least a part of the calcium carbonate particles formed into the reaction mixture are disintegrated.

5 6. The process according to claim 5, wherein the mixture is mixed with an impact mixer.

10 7. The process according to any of claims 1 to 6, wherein, for preparing calcium carbonate products, such as calcium carbonate suitable for paper coating, with a narrow particle size distribution, the reaction mixture is subjected to a mixing action, which disintegrates CaCO_3 crystals at the earliest after at least 15 minutes from the initial mixing of the components or when the mixture during the course of the reaction has become plasticized again.

15 8. The process according to any of the preceeding claims, wherein the reaction mixture containing hydrated calcium oxide and carbonate ions is formed in the initial stage of the process by mixing together in an impact mixer an aqueous suspension containing a calcium oxide-based raw material and an aqueous suspension containing carbonate ions.

20 9. The process according to any of the preceeding claims, wherein the carbonate ions are brought into the reaction mixture in the form of an aqueous solution of sodium carbonate.

25 10. The process according to claim 9, wherein the carbonate ions are also introduced into the reaction mixture in the form of carbon dioxide.

30 11. The process according to claim 10, wherein carbon dioxide is brought into the reaction mixture during the initial mixing stage in the form of pure carbon dioxide gas or in the form of a gas mixture containing carbon dioxide, said gas or gas mixture being fed into the mixing zone of the impact mixer.

12. The process according to claim 10 or 11, wherein carbon dioxide is introduced into the reaction mixture during the interruption of the reaction in the form of pure carbon

dioxide gas or as a gas mixture containing carbon dioxide. said gas or gas mixture being fed into the mixing zone of the impact mixer.

13. The process according to any of claims 1 to 7, wherein the carbonate ions are introduced into the reaction mixture in the form of carbon dioxide.

14. The process according to any of the previous claims, wherein the starting material containing at least partially hydrated calcium oxide is produced by

- grinding calcium oxide into a particle size which is less than 200 times the maximum diameter for 80 % of the crystals of the slaked lime, and
- the calcium oxide is slaked by mixing it with water, strong shear forces being applied to the mixture formed by calcium oxide and water.

15. The process according to claim 14, wherein the calcium oxide is slaked by mixing it with water in an impact mixer.

16. The process according to claim 14 or 15, wherein the calcium oxide is ground to the desired granular size in a vibratory cone crusher.

17. The process according to any of claims 14 to 16, wherein the calcium oxide is ground to a maximum particle size of 2 mm.

18. The process according to claim 1, wherein the crystal size of the calcium carbonate produced is controlled by adjusting the temperature to below +42 °C. when calcite crystals are produced, and to above +43 °C. when aragonite crystals are produced.

19. The process according to claim 9, wherein the concentrations of the starting materials are such that a solution of NaOH is produced by the causticizing reaction, which has a concentration of 6 % to 15 %.

20. The process according to any of the preceeding claims, wherein the calcium carbonate is filtered on a pressure filter.

21. An apparatus for preparing calcium carbonate, which apparatus comprises

- a reaction tank (11), wherein a calcium oxide-based raw material, which contains at least some hydrated calcium oxide, can be reacted with carbonate ions in an aqueous medium in order to produce calcium carbonate,
- feeding means (9, 10) connected to the reaction tank for the calcium oxide-based starting material and for an aqueous solution containing carbonate ions, and
- discharge means (12, 13) connected to the reaction tank for removing the calcium carbonate product from the tank.

characterized in that

- said feeding means are connected to an impact mixer (9), wherein the calcium oxide-based starting material and the carbonate ions containing aqueous solution can be mixed together before they are fed into the reaction tank (11).

22. The apparatus according to claim 21, wherein the impact mixer is provided with a feed nozzle for carbon dioxide gas or gas containing carbon dioxide, in order to bring carbon dioxide in contact with the aqueous slurry of the calcium oxide-based raw material.

23. The apparatus according to claim 21 or 22, wherein an impact mixer (12) is connected to the discharge means for interruption of the reaction between the hydrated calcium oxide and the carbonate ions.

24. The process according to any of claims 21 to 23, which further comprises a slaking unit (1 - 4) for calcium oxide, which unit is connected to the feeding means of the reaction tank and intended for preparation of an aqueous slurry containing hydrated calcium oxide. characterized in that said unit is formed by a crusher (2) for disintegration of calcium oxide and an impact mixer (3) connected to the outlet of the crusher, wherein the disintegrated calcium oxide can be brought into contact with water.

25. The apparatus according to claim 24, wherein the crusher is a vibratory cone

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crusher.

5 26. The process according to claims 21 to 25, wherein the outlet of the impact mixer (12) is connected to a pressure filter (16), which can be used for separating the solid matter from the aqueous slurry.

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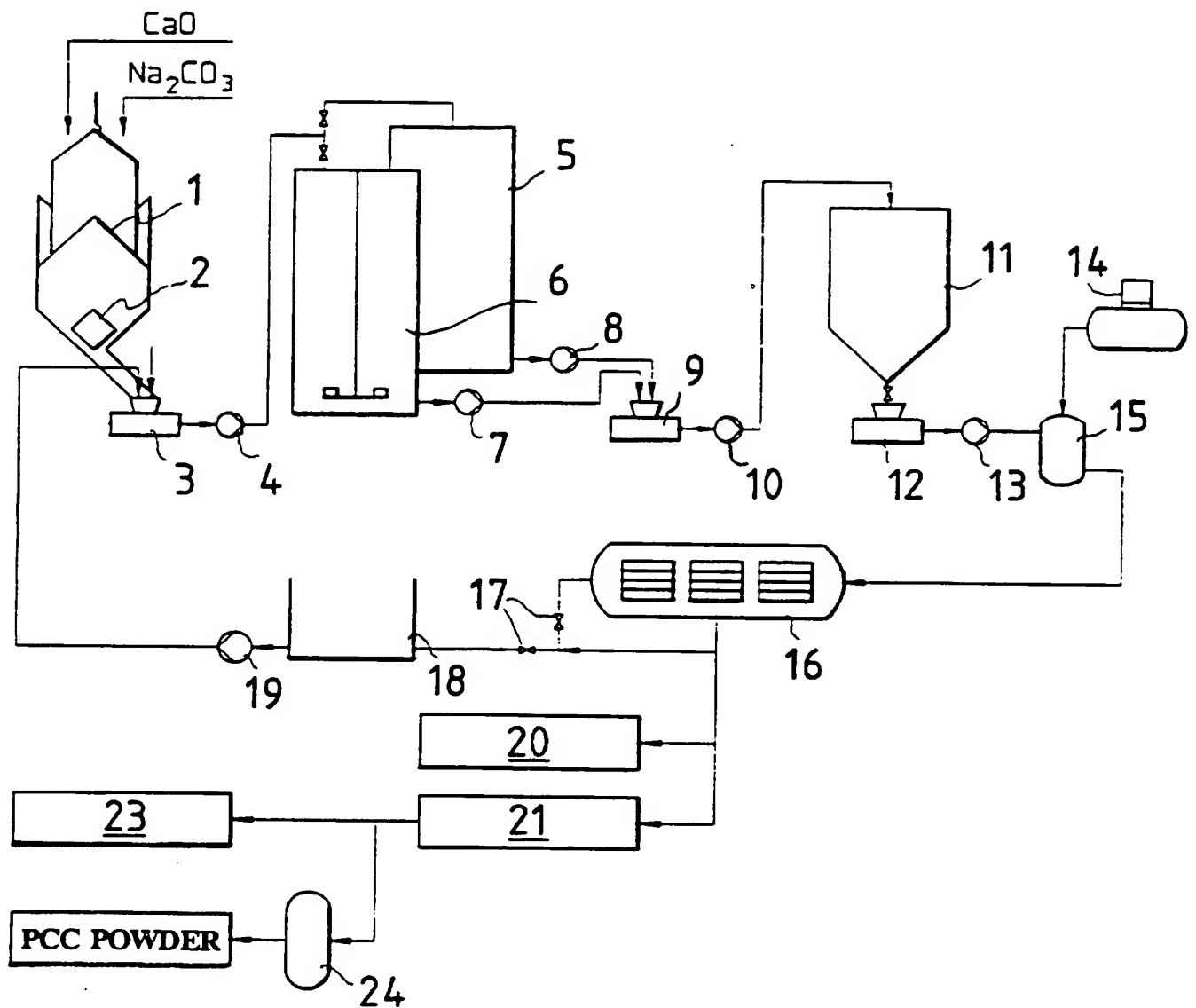


Fig. 1

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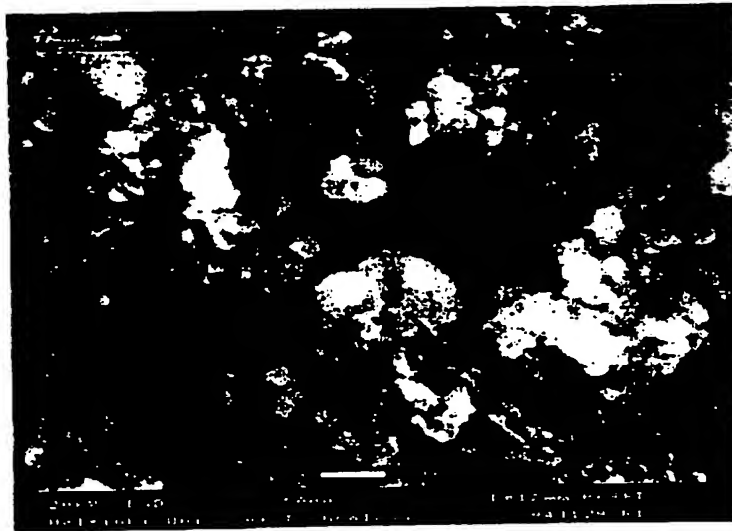


FIG. 2

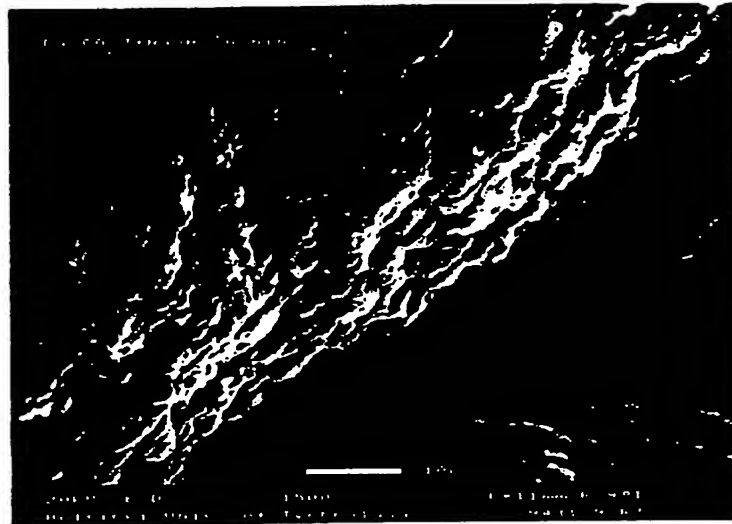


FIG. 3

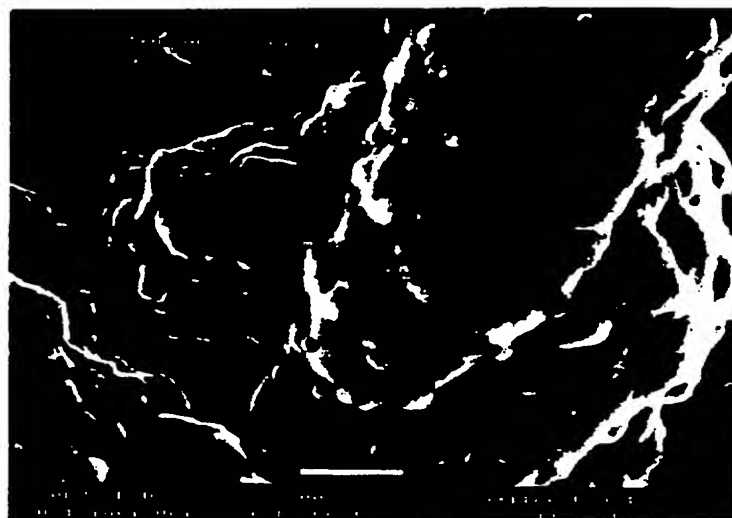


FIG. 4

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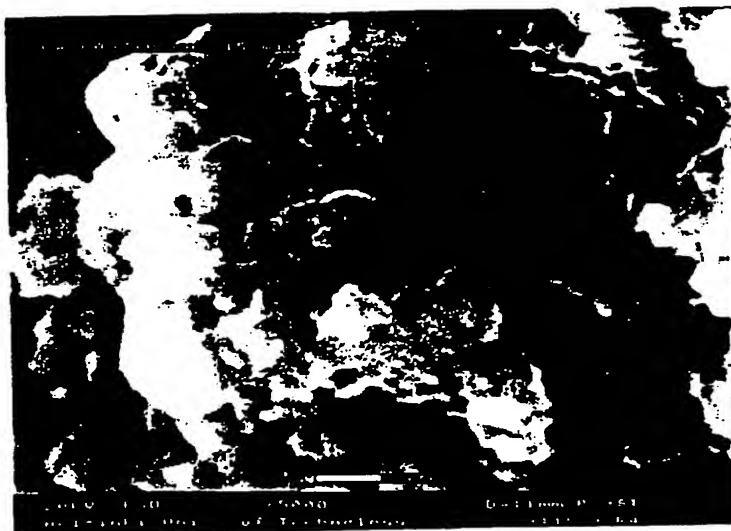


FIG. 5

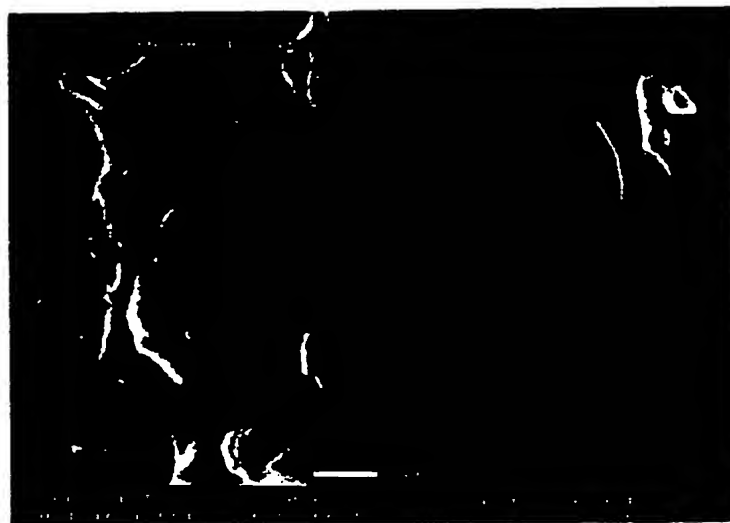


FIG. 6

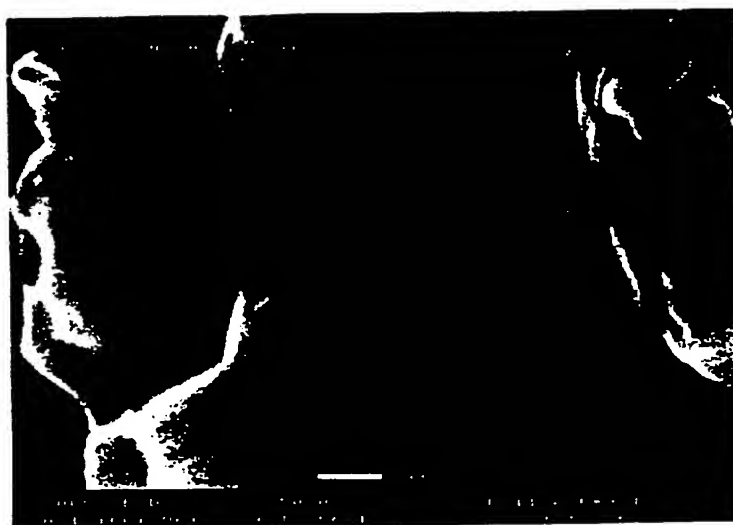


FIG. 7

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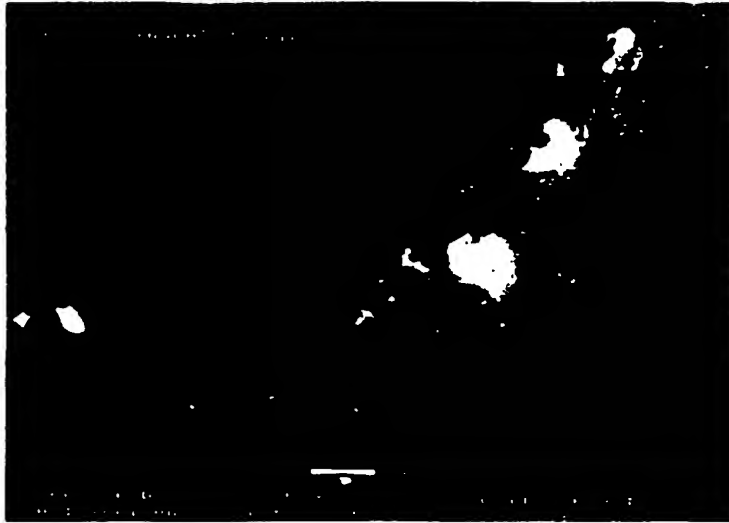


FIG. 8

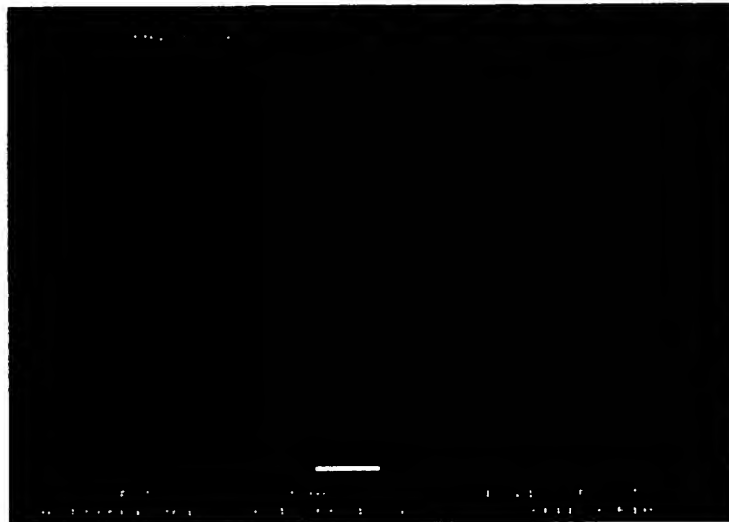


FIG. 9

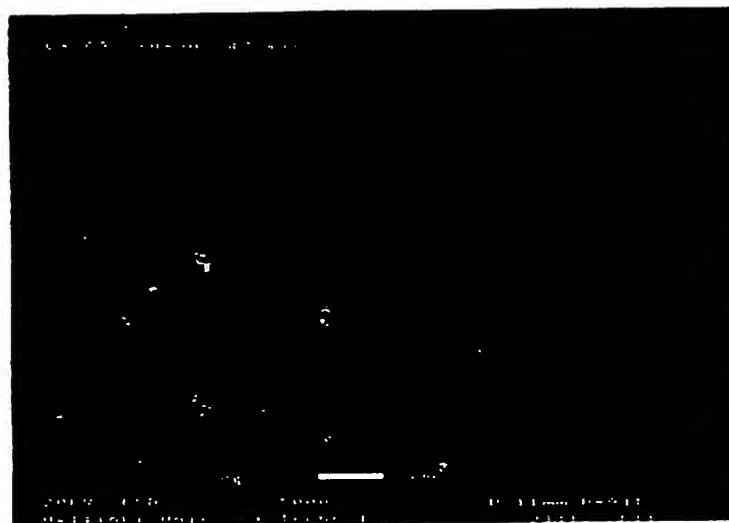


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI 96/00058

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C01F 11/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	WO 9312038 A1 (ADLER, PAUL, E.), 24 June 1993 (24.06.93) --	1-26
A	US 5342600 A (BLEAKLEY ET AL), 30 August 1994 (30.08.94) --	1-26
A	US 5364610 A (MERRIS, JR.), 15 November 1994 (15.11.94) -- -----	1-26

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex

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Date of the actual completion of the international search

17 April 1996

Date of mailing of the international search report

02 -05- 1996

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INTERNATIONAL SEARCH REPORT
Information on patent family members

01/04/96

International application No.
PCT/FI 96/00058

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9312038	24/06/93	AU-A- 3277193	19/07/93
		CA-A- 2125695	24/06/93
		EP-A- 0616602	28/09/94
		FI-A,D- 942797	25/07/94
		NO-A,D- 942218	28/07/94
		US-A- 5205493	27/04/93
US-A- 5342600	30/08/94	AT-T- 114143	15/12/94
		AU-B- 649721	02/06/94
		AU-A- 8526291	28/04/92
		CA-A- 2087857	28/03/92
		DE-D,T- 69105183	24/05/95
		EP-A,A,A 0480587	15/04/92
		SE-T3- 0480587	
		ES-T- 2064047	16/01/95
		GB-A,B- 2248229	01/04/92
		JP-T- 6501235	10/02/94
US-A- 5364610	15/11/94	WO-A,A- 9206038	16/04/92
		CA-A- 2125846	16/12/94
		FI-A,D- 942815	16/12/94
		SE-A,D- 9401906	16/12/94